

# BONDING COMPOSITIONS TO THE HARD TISSUE OF HUMAN BODY

The present invention relates to a bonding composition capable of bonding to the hard tissue of the human body and more particularly, to a bonding agent for medical or dental use capable of bonding to the hard tissue of the human body, such as bones and teeth.

Conventionally silver amalgam, such as an amalgam of silver alloy and mercury, and silicate cement have been used as restorative filling materials. The dental amalgam is excellent in physical properties, but it shows low bonding to teeth and it is insufficient in impact resistance, which tends to cause recurrent caries because of insufficient sealing of the margins of a filling to a tooth and in addition, entails the fear of exerting adverse influences on the human body from the viewpoint of toxicity. Further, silicate cement has a solubility and in addition, likewise it is low in bonding to teeth and is insufficient in marginal sealing. Moreover, it entails such shortcomings as intense pulpal irritation. Epoxy type resin-based filling material has been used, but it entails such drawbacks as inferiority in hardness and abrasion resistance and it is high in the water sorption.

Compositions consisting predominantly of bisphenol A-diglycidylmethacrylate (hereinafter called "Bis-GMA" for short) which is better in the compressive strength and water resistance than prior materials and is comparatively low in the pulpal irritation, and a great deal of inorganic filler and containing, as polymerization catalyst, a benzoylperoxide-tertiary amine catalyst (hereinafter called the composite resin for short) as disclosed in the U.S. Pat. Nos. 3,539,533; 3,066,112, 3,926,906, etc., for instance, came to be used as a restorative filling material for anterior teeth, in particular. But, for the reasons that in addition to the somewhat insufficient bonding of Bis-GMA, notwithstanding that a hydrophilic group-containing Bis-GMA is used, the joint use of a great deal of inorganic filler enhances the viscosity of the composite resin and worsens the wetting on the tooth surface, that composition has the serious shortcomings that it is poor in the bonding to dentin and enamel, which causes shedding of the filling material after filling the tooth and induces recurrent caries because it does not give a good marginal seal.

Further, proposals have recently been made of methods for using bonding agents consisting predominantly of Bis-GMA, but not containing the inorganic filler, for the improvement of the bonding of the Bis-GMA type composite resin, but their effect is not as yet fully recognized.

Other than that, developments have been made of adhesives consisting predominantly of  $\alpha$ -cyanoacrylate as a pit and fissure sealant or as an adhesive for orthodontics, but under the wet conditions that exist in the oral cavity, the bonding strength is lowered in a short period of time.

As mentioned above, no discovery has been made, up to the present time, of a bonding material having sufficient bonding strength to the hard tissue of the human body and, in addition, is capable of maintaining the bonding strength for a long time under such wet and temperature gradient-rich environments as in the oral cavity.

In view of such problems, the instant inventors studied bonding agents having excellent bonding strength to

the hard tissue of the human body which led to the accomplishment of the present invention.

The present invention is designed to provide a bonding material having a steadfast and durable bonding strength to the hard tissue of the human body.

Another purpose of the present invention is to provide an excellent bonding material which exhibits a steadfast and durable bonding strength for bonding operative dentistry and prosthetic dentistry material to the hard tissue of the human body, such as dental composite resin, and the hard tissue of the human body, without losing the characteristics of the operative dentistry and prosthetic dentistry material.

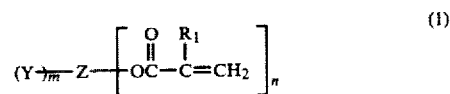
Still other purposes and merits of the present invention will be clear from the explanations which follow:

According to the present invention, the said purposes and merits of the present invention can be achieved by bonding compositions capable of bonding to the hard tissue of the human body consisting predominantly of a composition comprising

(A) 50-99.5% by weight of polymerizable acrylate esters, methacrylate esters, acrylamide derivatives or methacrylamide derivatives (hereinafter called the component A for short) possessing at least one group selected from the group consisting of carboxyl groups, epoxy group, amino group and hydroxyl group and

(B) 0.5-50% by weight of at least one organic metal compound selected from the group consisting of alkoxy-containing titanium compounds and silicon compounds (hereinafter called the component B for short).

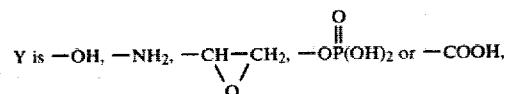
For the said acrylate esters or methacrylate esters used as the component A in the present invention any ones will do only if they possess at least one member selected from the group consisting of carboxyl group, epoxy group, amino group and hydroxyl group, but particularly preferred are those which are represented by following formula (1):



wherein

n is a positive integer of 1-3,

m is 1 or 2,



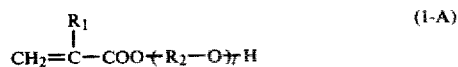
Z is a  $\text{C}_{1-25}$  organic group of (n+m) valence and

$\text{R}_1$  is a hydrogen atom or a methyl group.

In the said group Y endows the acrylate esters or methacrylate esters with hydrophilic property.

A-I. The following are more preferred examples of such acrylate esters and methacrylate esters.

(1) Compounds represented by following formula (1-A):



wherein

$\text{R}_1$  is a hydrogen atom or a methyl group,